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Comparative Studies of Electrochemical Behaviour of Carbon Nanotubes Obtained From Mustard Soot With Various Commercially Available Carbon Nanomaterials

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Abstract — It has been found that multiwalled carbon nanotubes (CS-CNT) can be produced in mass level, simply by pyrolysing mustard oil which was then derivatized with carboxylic acid (CS-CNT (acid)) and ammonia (CS-CNT (base)). A low cost electrode was fabricated on Teflon substrate with three silver wires which was coated with different types of carbon nanotube. A comparative study of electrochemical behaviour of the low-cost CS-CNT electrode has been carried out with the market procured single walled carbon nanotubes (SWCNT), multiwalled carbon nanotubes (MWCNT), pyrolytic graphite (PG) as well as with the standard screen-printed carbon nanotube electrode (std-CNT), by cyclic voltammetry in 0.1mM aqueous solutions of potassium ferricyanide and ferric chloride in presence of 0.1M sulfuric acid and 0.1M hydrochloric acid, respectively. The comparative study demonstrate that CS-CNT, obtained from mustard soot on the teflon substrate can be used as a low cost electrode in the electrochemical sensors and devices.

Keyword — Cyclic voltammetry, CSCNT, MWCNT, SWCNT, PG, electrodes

1. INTRODUCTION

Electrochemists are always in search of optimal electrode surfaces with the aim of producing electro catalytic responses, where the molecular engineering of an electrode surface is of paramount importance for the development of electrochemical devices. Extensive literature are available on chemically modified electrode for the electro analysis [1]-[4], but the common problems are instability, low sensitivity, cost and irreproducible thickness which may limit their applications. Taking into consideration that the analytical utility of an electrode material isgoverned by the electron transfer rate, back ground current, potential limits, mechanical properties and stability, carbon nanotube systems have proven as ideal materials that meet the desired properties for electro analytical uses [5]-[8]. Various configurations of carbon nanotube based electrodes are reported in the literature, by dispersingthe tubes with a binder[9], forming the nanotube equivalent of a carbon paste [10] which can be screen printed [11]-[13], drop coating onto an electrode without any binders, preparing a nanotube paper as electrode[14]-[15], abrasion onto the basal and edge planes of pyrolytic graphite [16]-[17] and modifying an electrode surface with C60.

The preparation of carbon nanotubes in mass level is in its infancy, and still there remains a number of challenges related to the preparation and modifications of carbon nanotube modified electrodes. Another problem lies in the fact that different kind of CNTs, produced from different sources possess the same problem of insolubility and a tendency of aggregation in most of the solvents due to the poor wetting properties of carbon nanotube, that is why the controlled modification of the electrode surface is quite difficult to achieve.

In this paper, a study has been carried out for the first time by fabricating a low cost Teflon electrode containing three silver wires, wherein mustard soot containing multiwalled carbon nanotubes (CS-CNT) as well as various type of carbon nanomaterials were mechanically mixed with polystyrene (PS) at 100°C, and dropped onto the electrode. We have synthesized the CS-CNT in mass level by pyrolyzing mustard oil, which was functionalized to have two forms viz. the carboxylated CS-CNT (acid) and the ammoniacal CS-CNT(base). These electrodes were then compared with commercially available single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), pyrolytic graphite (PG) and standard screen printed electrode (std-CNT). A comparative evaluation of all these electrodes has been carried out by studying the parameters such as anodic and cathodic peak potentials and anodic and cathodic peak currents under varied scan rates, using two redox systems

i.e. potassium ferricyanide and ferric chloride by cyclic voltammetry.

2. EXPERIMENTAL

2.1 Materials

All reagents purchased were of analytical grade. SWCNT, MWCNT and PS were purchased from Sigma-Aldrich. Silver wires were procured from Arora Matthey, of 99.999% purity. Solutions with the concentration of $9x10^{-4}$mol/l of potassium ferricyanide and of ferric chloride were prepared using 0.1 M H_2SO_4 and 0.1 M HCl as supporting electrolytes, respectively.

2.2 Preparation,functionalisationand characterization of CS-CNT

CS-CNT have been synthesized by a simple and age-old method of burning of mustard oil which was collected from the top portion of the flame, having temperature around 650ºC. The soot was then subjected to sequential purification. For carboxylic acid functionalization, the CS-CNTs were soaked in concentrated nitric acid overnight and then centrifuged. The CNTs were then washed with large amount of water and finally allowed to dry on standing in a boiling water bath. The dried mass was treated with distilled water and the mass was re-evaporated on a boiling water bath to dryness. The process was repeated until the traces of nitric acid were removed completely, and the mass was then finally dried under vacuum to yield CS-CNT (acid). The CS- CNT (acid) so obtained was sonicated in water to dissolve it and into it dilute ammonia solution was added to make it ammoniacal. The solution was allowed to stand for some hours and finally was evaporated on a boiling water bath. Once solidified, the mass was treated with distilled water and the insoluble portion was centrifuged out and was finally dried under vacuum to be used for the study as CS-CNT (base).

The morphology and microstructure of CS-CNT were studied by Scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analysis and were recorded with FEI Quanta 200 Hv and" Tecnai 20 G2" 200 kV STWIN used for Transmission electron microscopic (TEM) analysis [Figs. 1a and 1b].

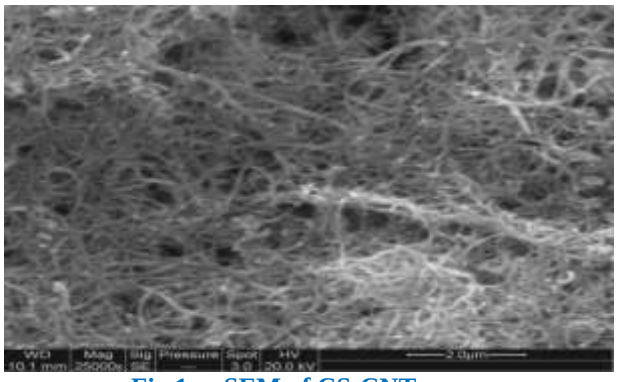


Fig.1a: SEM of CS-CNTs

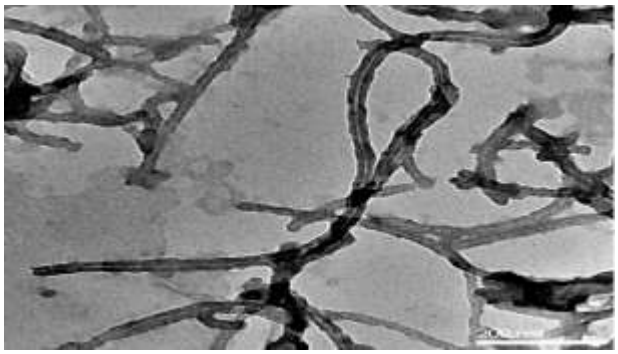


Fig.1b: HRTEM of CS-CNTs

2.3 Preparation of SWCNTs, MWCNTs, PG, CS-CNTs modified electrodes

The electrode containing different types of nanomaterials was fabricated on an insulating Teflon material and a three electrode cell was constructed using three silver wires of length (40cm) and width (1mm). Each conducting carbon material was dispersed in polystyrene solution in dichloroethane in 9:1 ratio, sonicated for 10 min and mechanically mixed at 100ºC using a mechanical stirrer. A drop of the slurry was deposited as a very fine thin film on the Teflon substrate covering two silver wires, and dried, which served as working and counter electrodes. The third silver wire was used as a reference electrode.

2.4 Cyclic Voltammetry

The cyclic voltammetric measurements were performed using the DropSens portable minipotentiostat (µStat100), employing a three electrode experimental set up. The minipotentiostat consists of a hand-held USB powered instrument, connected to a PC by means of an USB cable, for the use with electrochemical sensors or electrochemical cells. The instrument contains a microprocessor which controls the applied potential to the sensor and measures the current response. The CNT-polystyrene material, coated on a Teflon substrate served as the working as well as the counter electrode. Silver was used as the reference electrode and for all electrical contacts. The measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

A series of experiments were conducted to study the cyclic voltammetric responses of different types of carbon nanotubes towards 0.1mM potassium ferricyanide in 0.1M H_2SO_4 and 0.1mM ferric chloride in 0.1M HCl under varied scan rates. The electrochemistry of the two redox systems was compared using SWCNT, MWCNT, PG, CS-CNT (acid), CS-CNT (base) electrodes as well as screen-printed std-CNT electrode, supplied with the mini potentiostat.

Fig. 2 and Fig. 3 showed the summary of the observed redox responses of different carbon nanotube based electrodes towards potassium ferricyanide at different scan rates from 50mV to 200m. Among the various electrodes, commercially available screen-printed std-

CNT electrode which contain the carboxyl group modified multiwalled carbon nanotubes but from a different source, showed the highest degree of reversibility at all scan rates, with smaller peak-to-peak potential separation and the cathodic to anodic current ratio(i_c/ i_a), closer to unity. The CS-CNT (acid) electrode as well as the PG electrode performed better with respect to the reversibility compared to those observed from the market procured SWCNT and MWCNT. An interesting feature was observed in the case of CS-CNT (base) in comparison to its precursor, CS-CNT (acid) regarding its electrochemical response, which changed drastically in all scan rates.

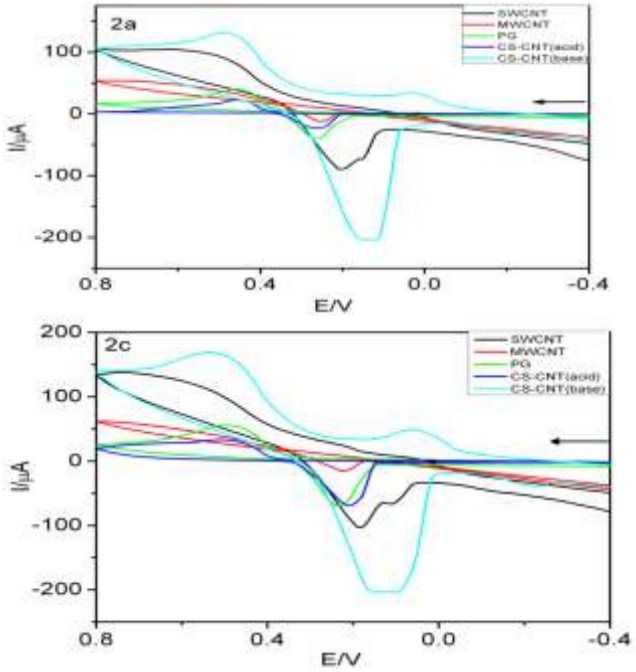
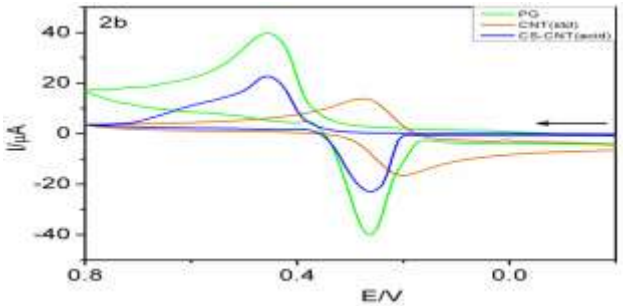


Fig. 2a,c: Cyclic voltammograms of $9x10^{-4}$ mol/l [K_3 $Fe(CN)_6$] for SWCNT, MWCNT, PG, CS-CNT (acid) and CS-CNT (base) at a scan rate of 50mV/s and 100mV/s, respectively



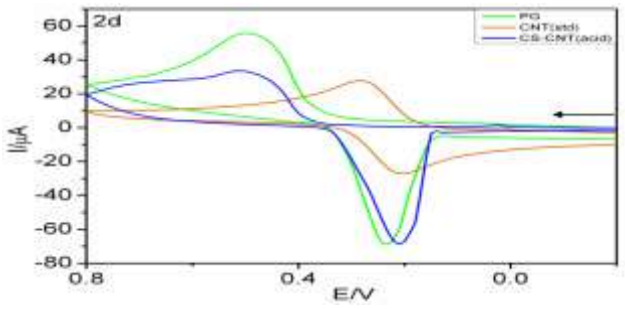


Fig.2b,d: PG and CS-CNT (acid) with std-CNT at a scan rate of 50mV/s and 100 mV/s, respectively

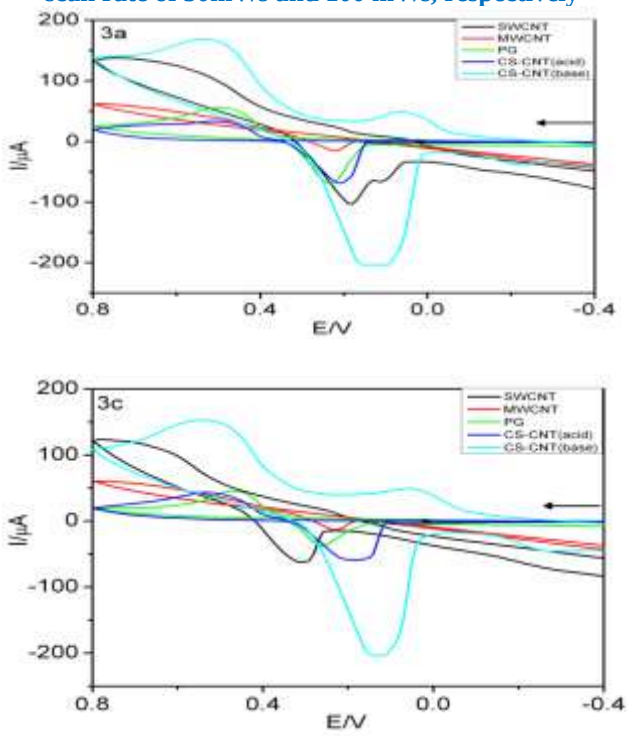
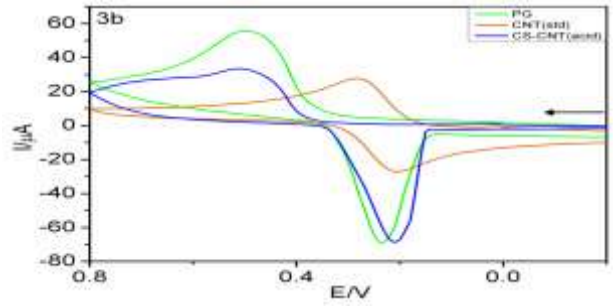


Fig 3a,c : Cyclic voltammograms of $9x10^{-4}$ mol/l [K_3 $Fe(CN)_6$] for SWCNT, MWCNT, PG, CS-CNT (acid) and CS-CNT (base) at a scan rate of 150mV/s and 200 mV/s, respectively



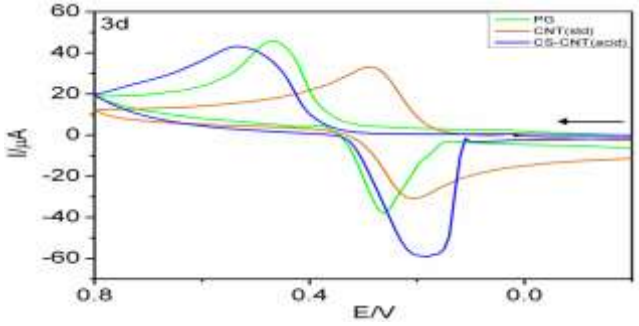
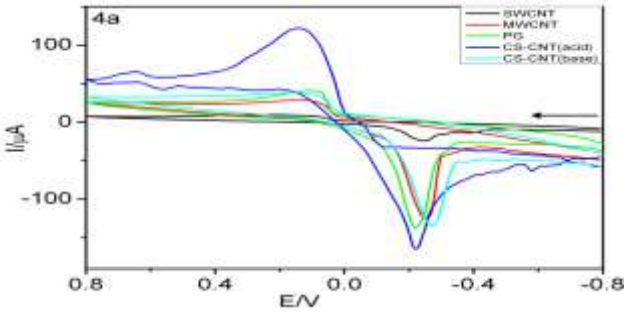


Fig 3b,d: PG and CS-CNT (acid) with std-CNT at a scan rate of 150mV/s and 200 mV/s, respectively

In Figs.4 and 5, a different trend was observed with the second redox couple ferric chloride. In contrast to the results obtained from potassium ferricyanide, a completely different electrochemical behavior was observed where consistently the cathodic peak potential shifted towards negative value in case of all the electrodes. All the carbon nanotube modified electrodes were found to move towards more irreversible character except in the case CS-CNT (acid), where it displays reversibility. CS-CNT (acid) showed excellent reversibility, with smaller peak-to-peak separation and the i_c/ $i_a$ratio being closer to unity. In the case of ferric chloride, both the anodic and cathodic peak currents observed were very low in SWCNT electrode, but was found to be significantly higher in the Teflon electrodes coated with MWCNT, PG, CS-CNT (acid) and CS-CNT (base). It was highly interesting to observe the voltammetric response of CS-CNT (base), which in contrast to the acid modified CS-CNT (acid), showed the largest separation in peak potential. A second important feature was observed for CS-CNT (base) where the anodic and the cathodic peak current were found to be consistently higher for the entire scan rate.

All these data showed that the carboxylic functionalized CS-CNT (acid) on Teflon substrate have a clear advantage over the electrodes modified with commercially available single walled and multi walled carbon nanotubes from the perspective of the electron transfer species in aqueous solutions. The use of the CNTs-insulating PS mixture constitutes a simple and cheap electrode material that exhibits the advantage of generating a fresh electrode surface by only polishing with solvent every time that is needed for successive experiments. This basic knowledge could be helpful in the design, construction and optimization of carbon nanotube based electrodes.



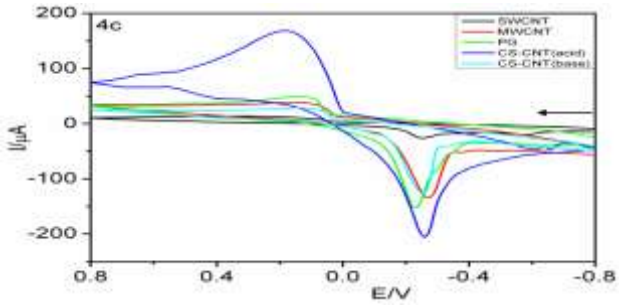
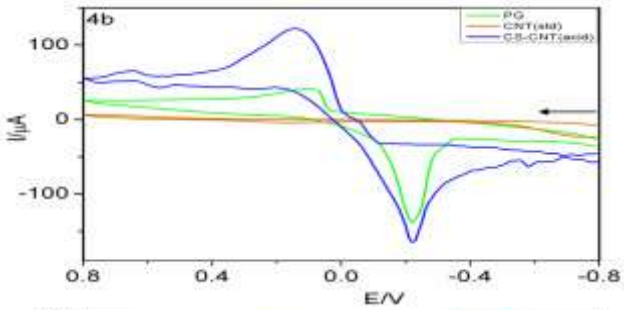


Fig. 4a,c: Cyclic voltammograms of $9x10^{-4}$ mol/l $FeCl_3$ for SWCNT, MWCNT, PG, CS-CNT (acid) and CS-CNT (base) at a scan rate of 50mV/s and 100 mV/s, respectively



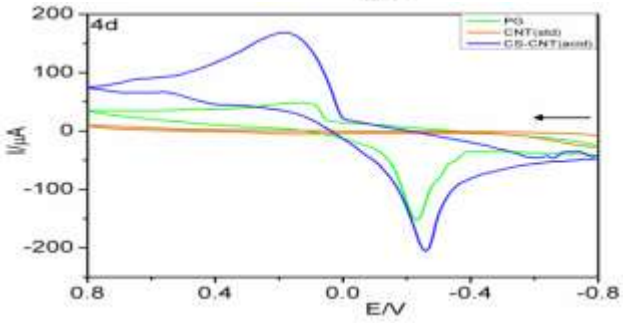


Fig.4b,d: PG and CS-CNT (acid) with std-CNT at a scan rate of 50mV/s and 100 mV/s, respectively

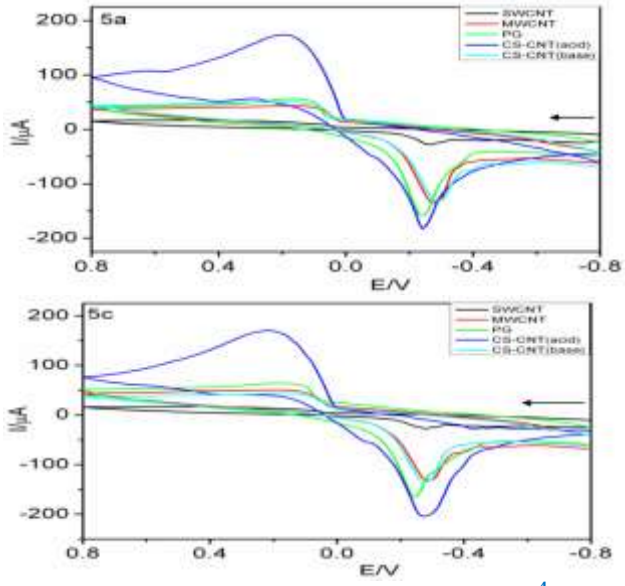


Fig. 5a,c: Cyclic voltammograms of $9x10^{-4}$ mol/l $FeCl_3$for SWCNT, MWCNT, PG, CS-CNT (acid) and CS-CNT (base) at a scan rate of 150mV/s and 200 mV/s, respectively

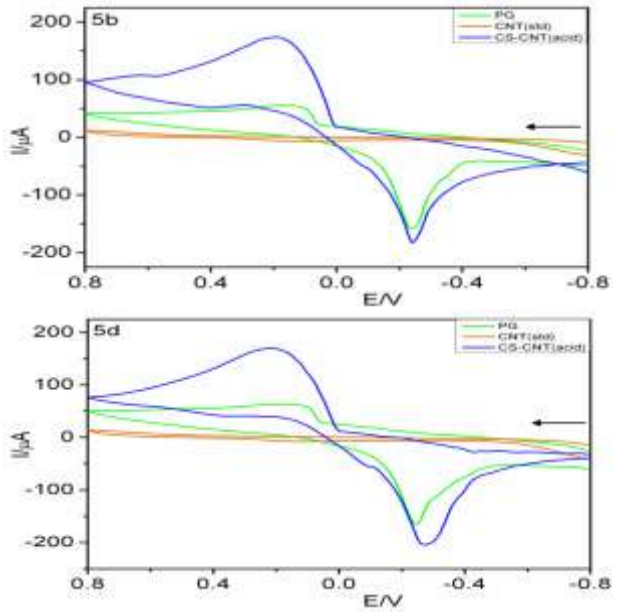


Fig.5b,d: PG and CS-CNT (acid) with std-CNT at a scan rate of 150mV/s and 200 mV/s, respectively

4. Conclusion

Apart from the ongoing research towards the modification of CNT based electrodes, from the economic point of view, it is necessary to have a method which can produce CNTs in a mass level. With this aim, for the first time we have carried out a study and tried to explore the electrochemical behaviour of multiwalled carbon nanotube electrodes, produced from a very simple and cheap process of pyrolysing mustard oil, its two derivatives, various types of market procured carbon nanotube modified electrodes, pyrolytic graphite based electrode as well the screen printed standard electrode towards two redox couple, in order to have a better understanding of the requirement of conducting carbon materials as electrochemical probes. The overall study implies that the carboxyl-modified CS-CNT (acid) electrode showed promising electrochemical activity towards both the redox couple, so no doubt, if it can conveniently replace the commercially available multi walled CNT modified electrodes, due to simplicity of preparation, low cost and relative advantages of reactivity.

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